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THE COMBINED EFFECTS OF ULTRAVIOLET RADIATION AND VACUUM ON THE ULTIMATE TENSILE PROPERTIES OF POLYMETHYLMETHACRYLATE

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INTRODUCTION

The effects of the combined constituents of the space environment on the mechanical properties of polymers in the glassy state and in the brittle tough transition region are of interest to the NASA. The degradation mechanism of polymethylmethacrylate, when exposed to ultraviolet radiation in vacuum, at temperatures in the range of 160° to 220°C, has been reported by Melville[1] to consist of depolymerization producing only methylmethacrylate monomer. Stress relaxation and fracture behavior of polymethylmethacrylate have been studied by Tobolsky[2] and Berry[3], respectively. At the Ames Research Center, samples of polymethylmethacrylate sheet stock were exposed to ultraviolet radiation in vacuum at 100°C. This is the maximum useful temperature for application of this polymer. The volatile products of this degradation were identified, and the changes in molecular structure of the exposed polymer were characterized.

On the basis of Melville's[1] observations, one would expect both an alteration in surface properties because of the large extinction coefficient of polymethylmethacrylate at wavelengths below 2700A° and plasticization of the bulk polymer due to monomer production.

Of the several mechanical properties studied at Ames, yield stress could be measured most accurately and was the most reproducible parameter which showed a definite effect of the simulated constituents of the space environment. Specific studies were made, therefore, on the effects of irradiation dose, surface defects, plasticizer (monomer) content, strain rate, and tensile test temperature, on the observed yield stress.

EXPERIMENTAL

Samples of 1/32" Plexiglas UV AII sheet stock were irradiated at a pressure of [illegible]$^{-6}$ Torr with the total flux available from a General Electric UA-2 mercury vapor lamp. In these experiments, the output of this lamp was approximately equivalent to one solar constant in the wavelength region from 2000 to 2700 $^{\circ}$A. The temperature of the samples was maintained at [illegible] $^{\circ}$C *at print/cage* within $\pm 2^{\circ}$C with a gradient not greater than 6°C. *through 1/32"* The volatile products produced during this irradiation were trapped and identified mass spectrometrically.

Thin films for characterizing molecular weight changes at surfaces were obtained by solvent casting of dilute solutions of Plexiglas sheet stock dissolved in methyl ethyl ketone. The viscosity average molecular weights of these films were determined.

Standard ASTM-D-638 tensile specimens were cut from 1/32" sheet stock after irradiation. Tensile tests were performed at various constant strain rates from 0.0029 to 2.9 in/in/min. The test specimen temperature was maintained within $\pm 1^{\circ}$C and was varied over a range from -50° to 90°C. After failure of the specimens, photomicrographs of surface damage effects and measurement of crack depths were taken with a metallograph.

Absorption of methylmethacrylate monomer was induced by heating the 1/32 samples in a closed container to 76°C, at which point monomer vapor was introduced. The final weight of absorbed monomer was stabilized by placing the exposed samples in a heated vacuum desiccator at their approximate glass temperature for 24 hours.

RESULTS AND DISCUSSION

Only methyl methacrylate and trace amounts of moisture were obtained from samples irradiated at 100°C, in agreement with Melville's observation at higher temperatures. A change in viscosity average molecular weight from 3.16 x 10[illegible] to [illegible].52 x 10^4 was observed with 1 mil films in one hour under the same conditions. This molecular weight includes the monomer trapped in the film and is characteristic of the molecular structure of the surface of the thick specimens.

Typical decreases in yield stress as a function of irradiation time at constant ultraviolet flux and at three different strain rates are given in figure 1. These yield stresses were measured at 22°C and show a decrease of as much as 20 percent.

Surface defects and plasticization resulting from monomer production were investigated separately to determine the contribution of each to the observed decrease in yield stress.

A section of a sample which was irradiated for six hours and tested at 2.9 in/in/min at 22°C is shown in figure 2. The crater and surrounding surface ripples are believed to be produced by buckling of the surface due to stress caused by an increase in specific volume in the surface. This surface volume change is consistent with our observation of the decrease in molecular weight of the thin films.

Sufficient energy is available at the time of the buckling to expel a particle from the surface. After the entire surface is buckled, no more craters are formed. In figure 2, the failure plane indicated by the boundary between the two halves of the specimen is normal to the principle stress. The failure crack propagates from the rim of the crater to the edge of the specimen. Similar initial crack sites are observed in all specimens tested at 22°C or at lower temperatures.

The yield stress decrease after six hours of exposure, which amounts to approximately [illegible] percent as shown in figure 1, is concurrent with the formation of [illegible] craters which have an average depth of 0.004 in. This rapid yield stress decrease correlates very closely with the decrease observed by Berry [illegible] similar strain rates and an induced crack of the same depth.

The failure [illegible] site in the necked down region of a specimen irradiated for six hours and tested at 70°C at 0.0029 in/in/min is shown in figure 3. The yielding and consequent failure is similar to the Luder's line phenomena in [illegible] metals. These lines follow the narrow surface separations.

Additional exposure beyond the first six hours produced continued deterioration of the surface but did not increase crater depth. Hence, the further steady state decrease in yield stress amounting to about 0.20 percent per hour of the original yield stress may be attributed to changes in molecular structure of the bulk polymer.

In figure 4, the changes in the observed yield stress for four different strain rates at 22°C are given as a function of weight fraction of monomer induced by absorption. The decrease in yield stress is essentially linear with increasing monomer content to a weight fraction of monomer of about 0.10, at which concentration the yield stress is decreased by 40 percent.

In figure 5, it is shown that the steady state yield stress decrease in the irradiated specimens corresponds to an increase in the weight fraction of monomer of 0.0004/hr. Therefore, the steady state decrease in yield stress may be caused by plasticization due to an increasing amount of trapped monomer. In figure 5, the difference in yield stress between the dashed and solid lines is thought to be due to surface changes.

As part of the study of the effect of strain rate and temperature on yield stress, it was found that the yield stresses, when plotted as a function of strain rate and temperature, could be shifted parallel to the strain rate axis in either direction to become components of a "master curve." This is similar in principle to the shifts made by Tobolsky[2] to construct a stress relaxation master curve and, more recently, by Smith[5] to construct a failure envelope for elastomers above the glass transition temperature. The upper portion of this master curve is shown in figure 6 and indicates that the upper limit of the yield stress will be approximately 19,000 psi. The master curve is bounded at its lower limit by the flow stress of the polymer. It was experimentally verified that the shape of the master curve is unique regardless of irradiation dose or plasticizer content. The magnitude of the strain rate shift which must be applied to the yield stresses (which are measured at various temperatures and strain rates) is shown in Table 1 and figure 8.

Also included in Table 1 and figure 8 are data from irradiated and monomer absorption specimens tested at Ames, stress relaxation shift magnitudes reported by Tobolsky[2] and shift factors measured from tests conducted by Knowles and Dietz[4]. Sherby[6], in an analogy with the behavior of metals, foresaw that there was an interrelation between strain rate and test temperature. The shape of the shift factor curve, as shown in figure 8, also appears to be unique. Preliminary data shows that the temperature shift factor curves for various plasticizer concentrations superpose when referenced to the glass transition temperature.

If the yield stresses from the master curve are plotted on a semi-log plot, as shown in figure 7, the variation in yield stress as a function of strain rate may be approximated by a line and represented by:

$$\sigma_y = K \ln \left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_c} a_T \gamma \right) \tag{1}$$

where

σ_y = Yield stress psi

$\dot{\varepsilon}$ = Strain rate in/in/min

a_T = Temperature shift factor

γ = Plasticizer shift factor

K and $\dot{\varepsilon}_c$ = Constants

From figure 8, $K = 668$ psi and $\dot{\varepsilon}_0 = 1.8 \times 10^{-9}$ in/in/min for polymethylmethacrylate (Plexiglas).

The plot of the strain rate shift factor shown in figure 8 may be approximated by a straight line which has the equation

$$a_T = 10^{(1.60 - 0.0727\, T^\circ C)} \qquad (2)$$

(referenced at 22°C) and is applicable from -25°C to 100°C.

The yield stresses plotted as a function of weight fraction of monomer and strain rate in figure 9 were used to calculate the magnitudes of the plasticizer shift factor, γ, which is plotted in figure 10 as a function of weight fraction of monomer. Note that the stresses in figure 9 do not appear to fit a master curve as precisely as might be expected. This effect is due to limitations imposed by the experimental technique for adding monomer to the test specimens. Figure 10 also contains the curve which shows the plasticizer shift factor measured from the data of Knowles & Dietz[4]. From figure 10 the dependence of the plasticizer shift factor, γ, on the weight fraction of plasticizer, w, may be written as:

$$\gamma = 10^{cw} \qquad (3)$$

where

$c = -33.8$ for methyl methacrylate

$c = -16.67$ for dibutyl phthalate

and

$0 \leq w \leq 0.20$

Equations 1 through 3 can, therefore, be used to predict the yield stress of polymethylmethacrylate at strain rates which may not be readily available or to design for specific yield stresses. Equation 1 may be assumed to be valid if it gives yield stresses in the range from 3,000 to 19,000 psi for any combinations of strain rate, temperature and plasticizer contents which are within the limits of applicability of equations 2 and 3.

It is expected that the foregoing concepts should be applicable to other polymers below their glass transition temperatures in the same manner as the unique behavior above the glass transition temperature has been shown by Williams, Landel, and Ferry[7] and others to apply to all elastomers.

References

1. P.R.E.J. Cowley and H. W. Melville, Proc. Roy. Soc. (London) A 210, 461 (1952); A 211, 320 (1952).
2. J. Bischoff, E. Catsiff and A. V. Tobolsky, J. Am. Chem. Soc. 74, 3378 (1952).
3. J. P. Berry, J. Polymer Sci. 50, 107 (1961)
4. J. K. Knowles and A.G.H. Dietz, Trans. A.S.M.E. 77, 177 (1955)
5. T. L. Smith, SPE JOURNAL, Vol. 16, No. 11, 1, (1960)
6. G. D. Sharby, Trans. A.S.M.E. 77, 185 (1955)
7. M. L. Williams, R. F. Landel, and J. D. Ferry, J. Am. Chem. Soc. 77 3701 (1955)

TABLE 1

Temperature Shift Factors

Temperature °C	Non-Irradiated	18 Hrs. of Irradiation Each Side	Monomer Wt. Fraction of 0.0298	Knowles & Dietz Data[4]	Tobolsky[2] Stress Relaxation Data
100°	-6.2				-5.70
92					-4.75
90	-5.4				
80					-4.3
75			-3.25	-4.5	
70	-3.4	-3.50			
60					-3.4
50	-2.4		-2.0	-2.1	
40					-1.3
25				-0.2	
22	0	0	0	0	
0	1.6		1.5	-1.65	
-25	3.1	2.5	3.0	-2.65	
-50	4.2		3.9		

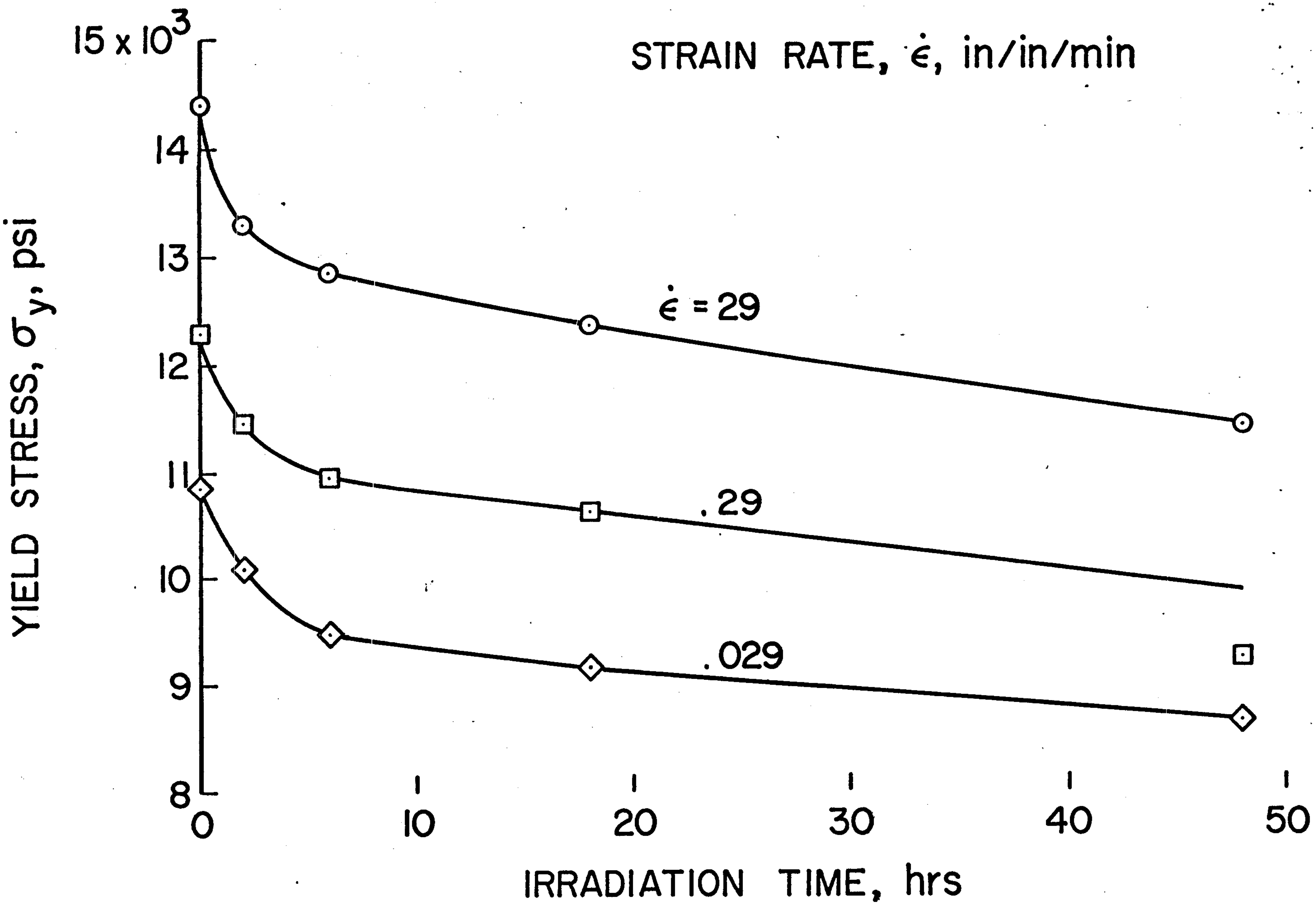

Figure 1. - The effect of strain rate and irradiation time on yield stress of polymethylmethacrylate at 22°C.

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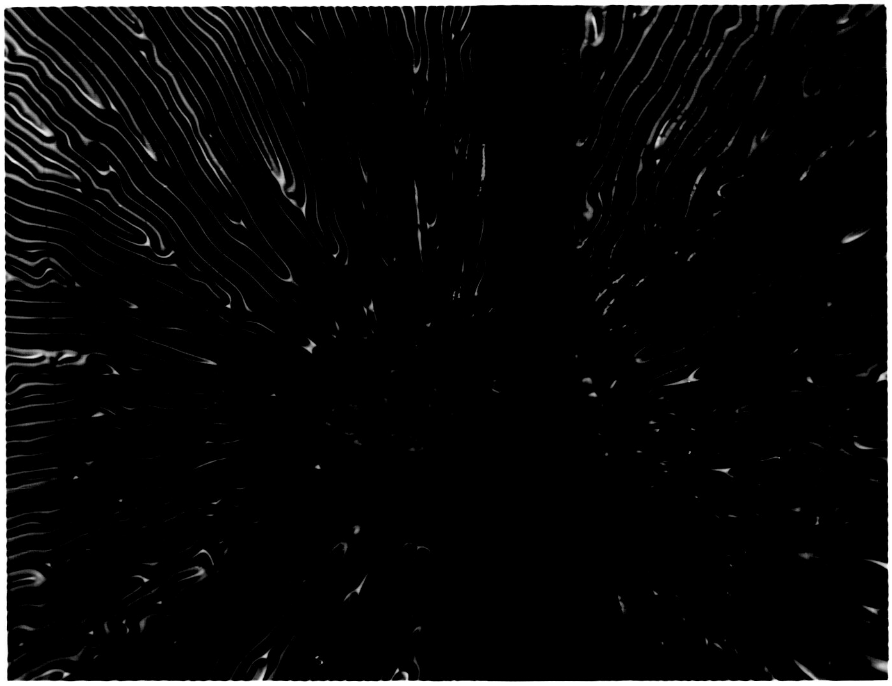

X150

Figure 2. - 150 x photomicrograph of polymethylmethacrylate showing brittle failure of specimen irradiated for 6 hours and tested at a strain rate 0.029 in/in/min and 22°C.

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X68

Figure 3. - 68 x photomicrograph of polymethylmethacrylate showing ductile failure and specimen irradiated for 6 hours and tested at a strain rate of 0.0029 in/in/min and 22°C.

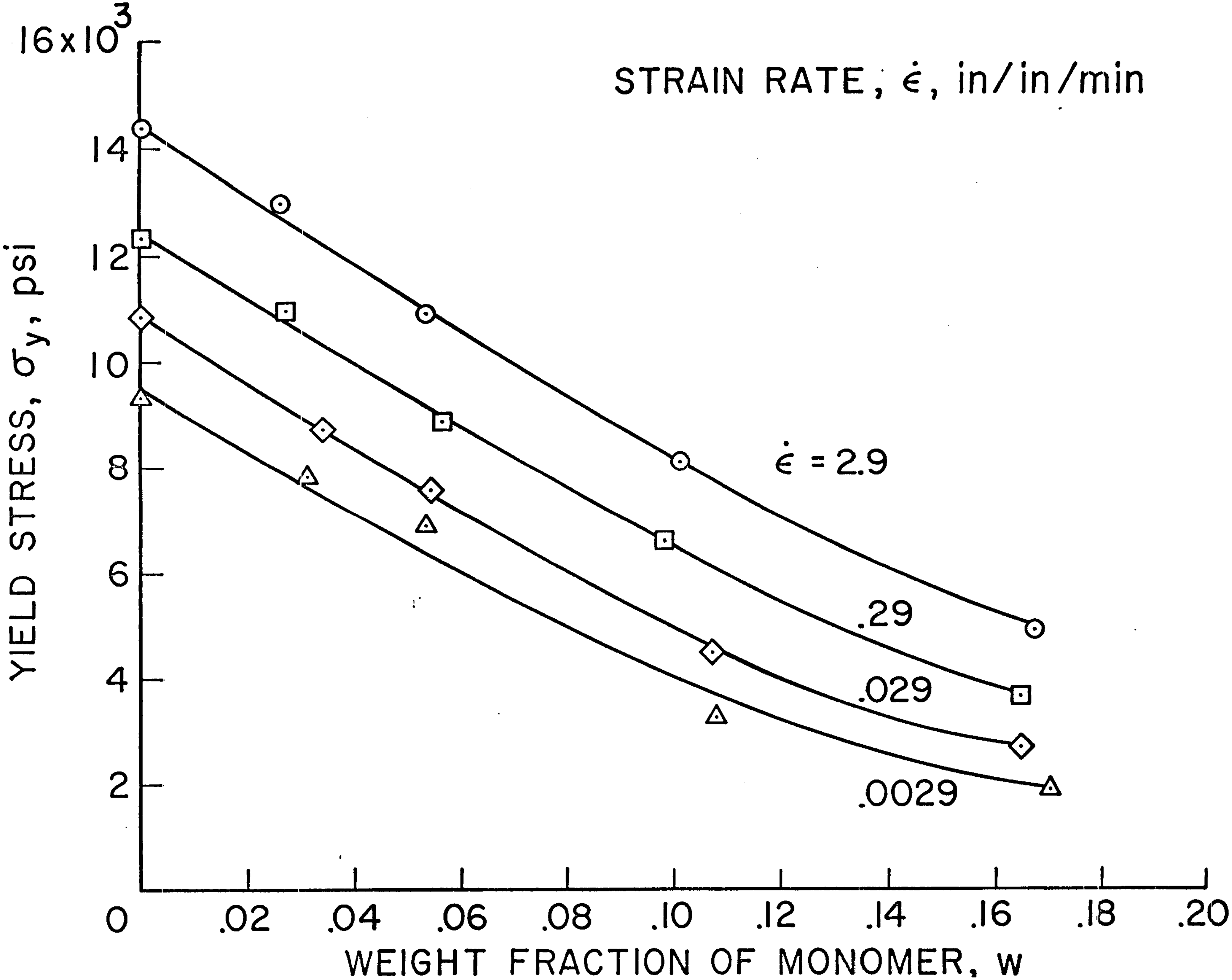

Figure 4. - The effect of strain rate and weight fraction of monomer on yield stress of polymethylmethacrylate at 22°C.

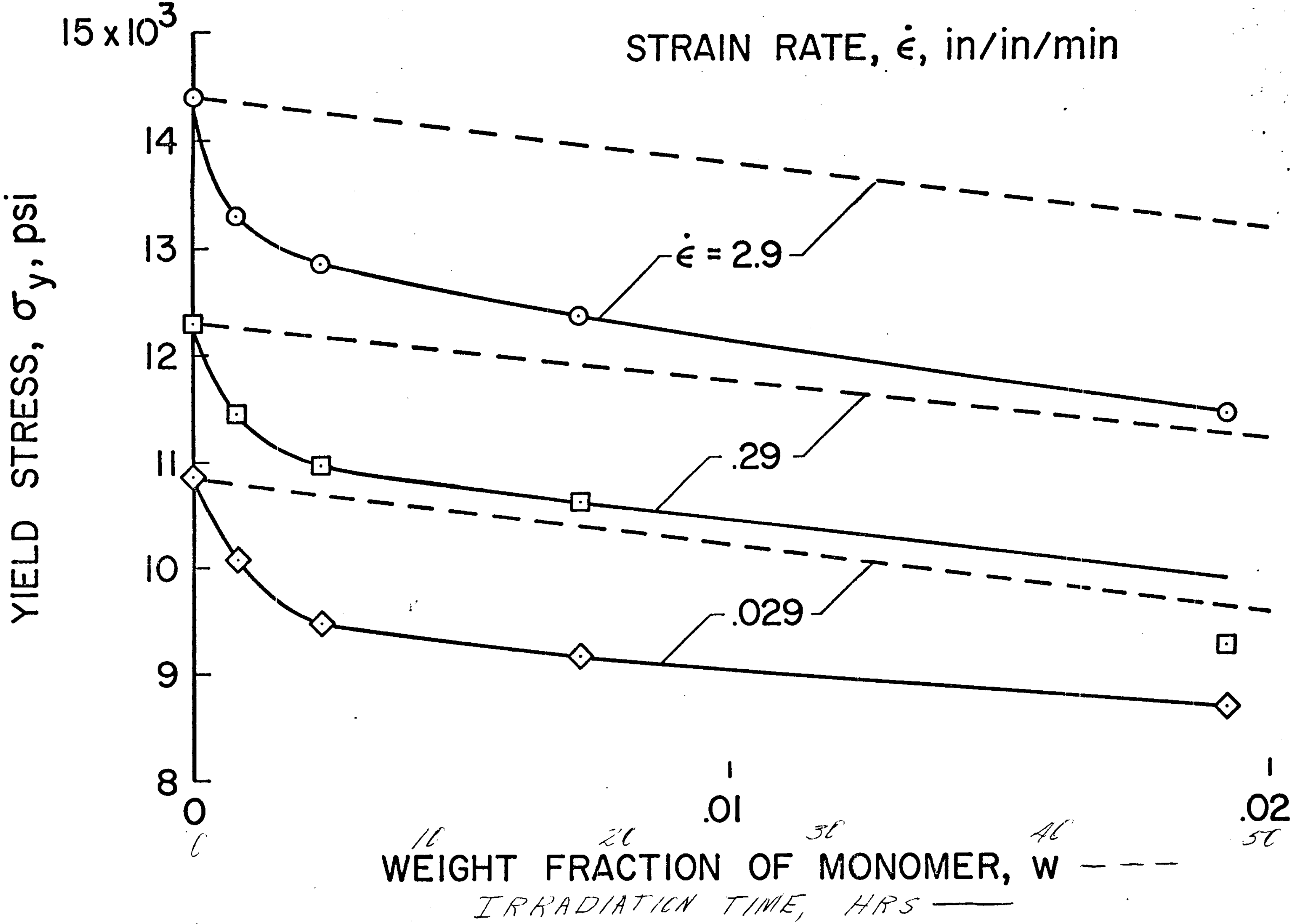

Figure 5. - Comparison of yield stresses of irradiated and absorbed monomer specimens of polymethylmethacrylate to show similarity of steady state decrease of yield stress:

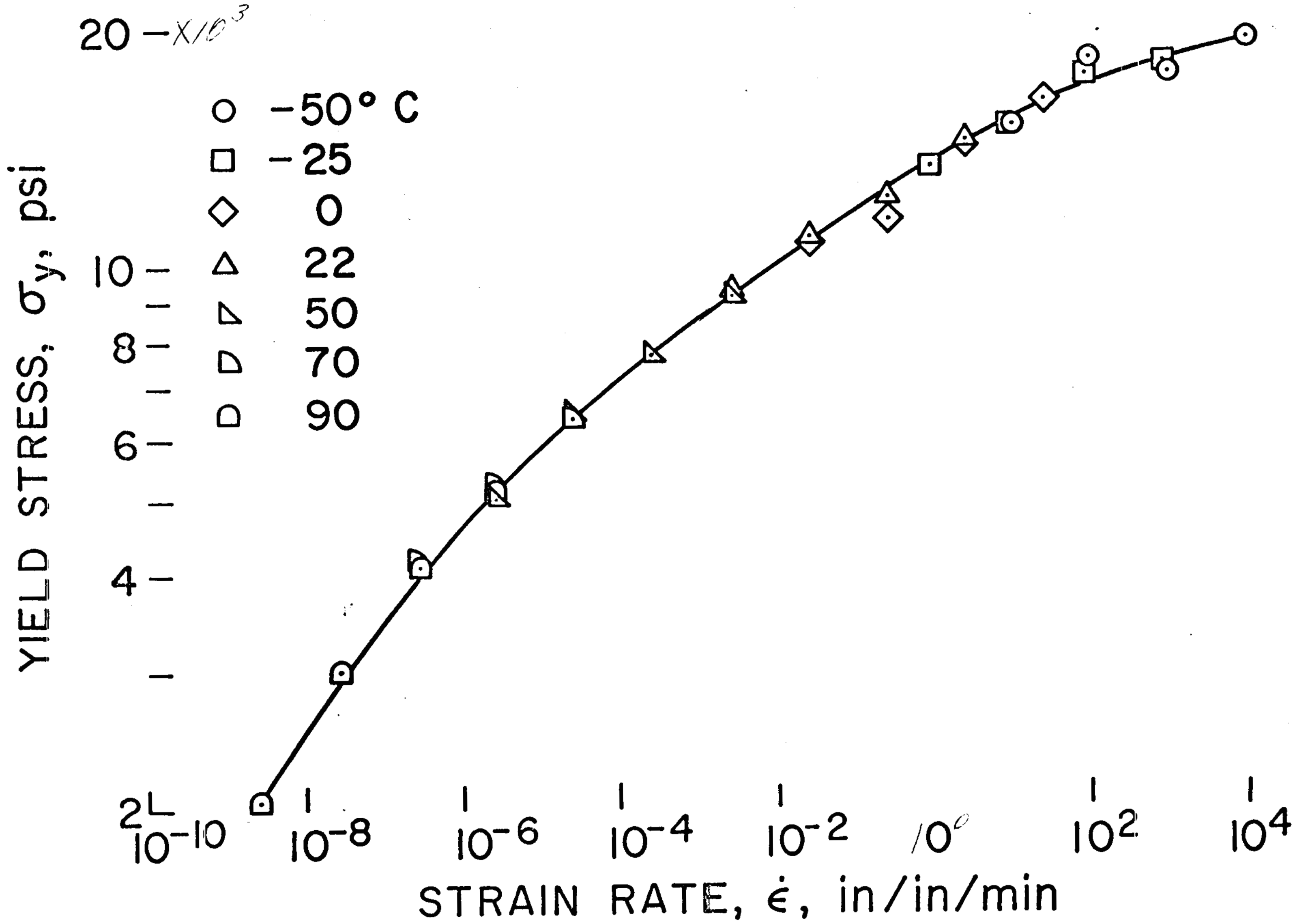

Figure 6.- Yield stress of polymethylmethacrylate as function of the shifted strain rate to give the "master curve" (referenced at 22°C).

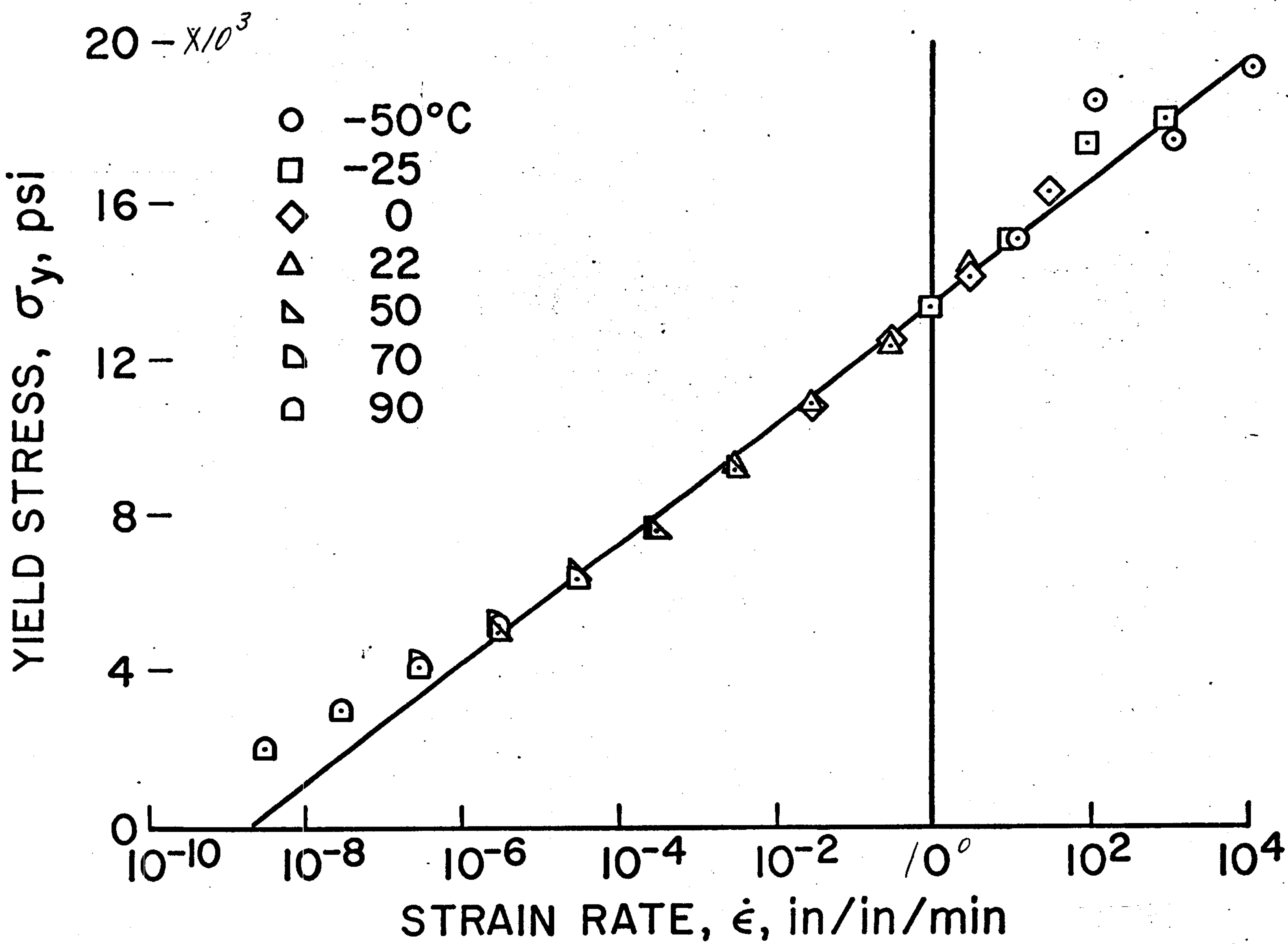

Figure 7. - Yield stress of polymethylmethacrylate as a function of the shifted strain rate (referenced at 22°C) for derivation of equation 1.

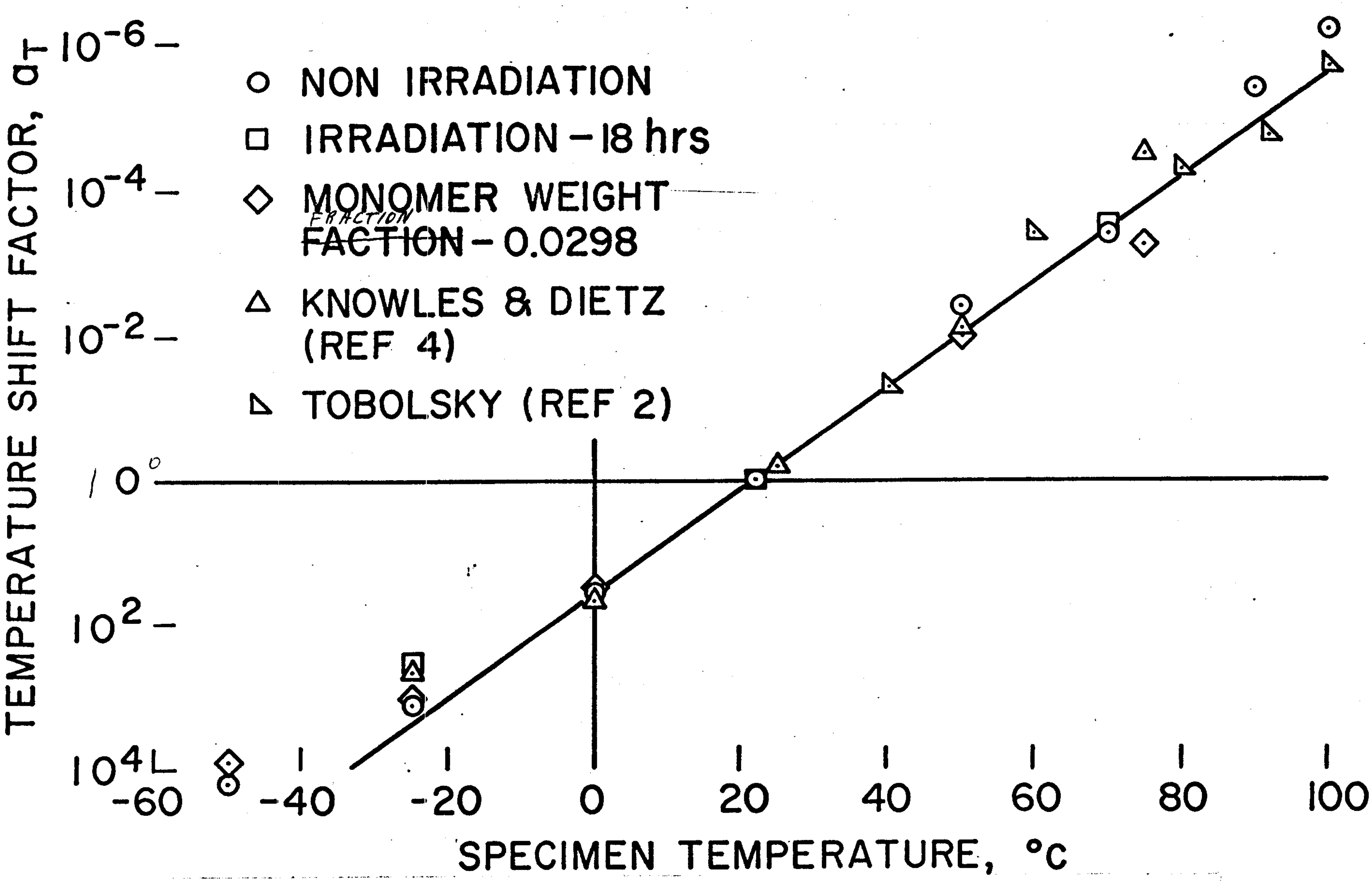

Figure 8. - The temperature shift factor for polymethylmethacrylate as a function of temperature (referenced at 22°C) for derivation of equation 2.

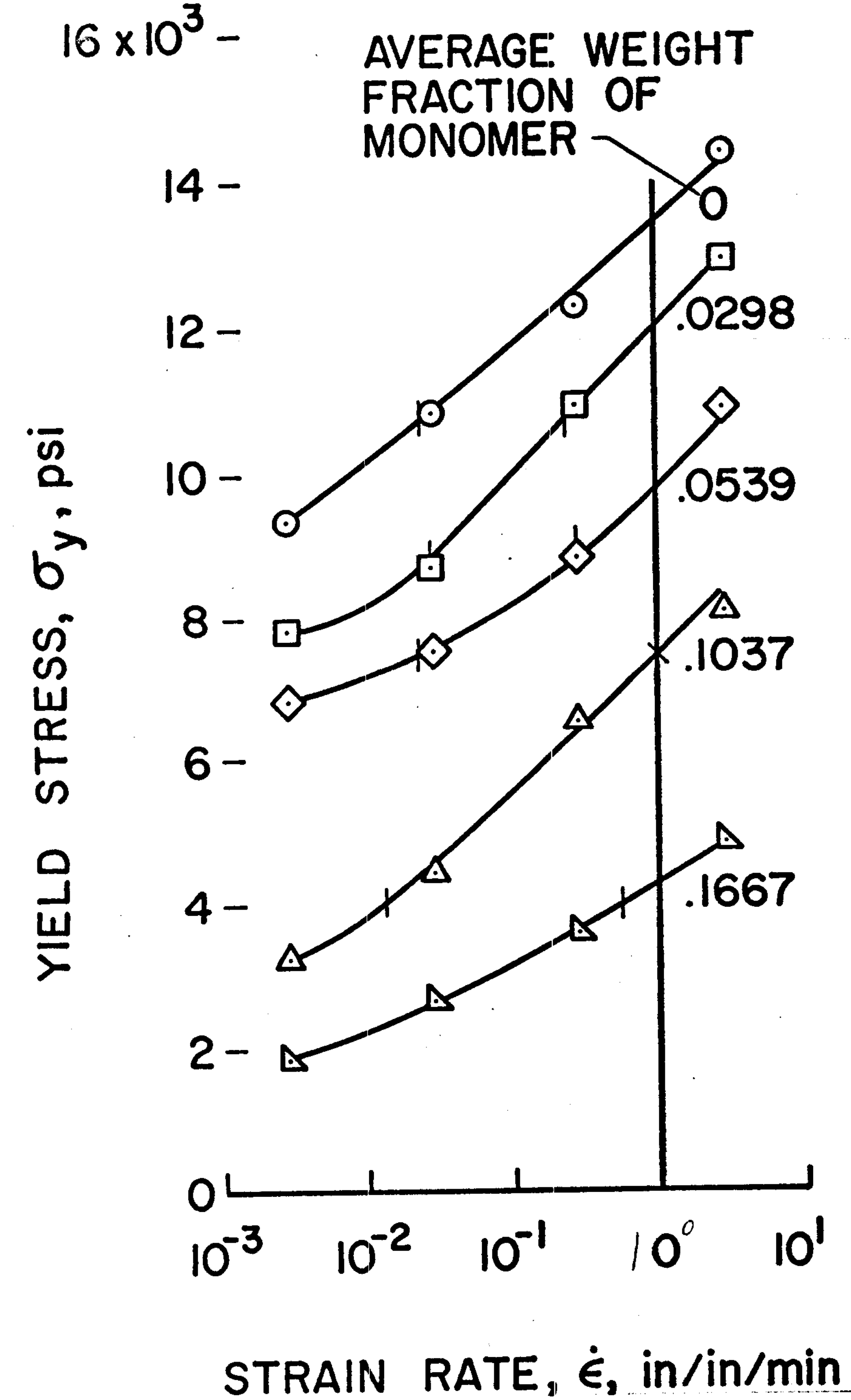

Figure 9. - The effect of strain rate and weight fraction of monomer on yield stress of polymethylmethacrylate at 22°C to sh[illegible]e measurement of the plasticizer dependent[illegible]t factor.

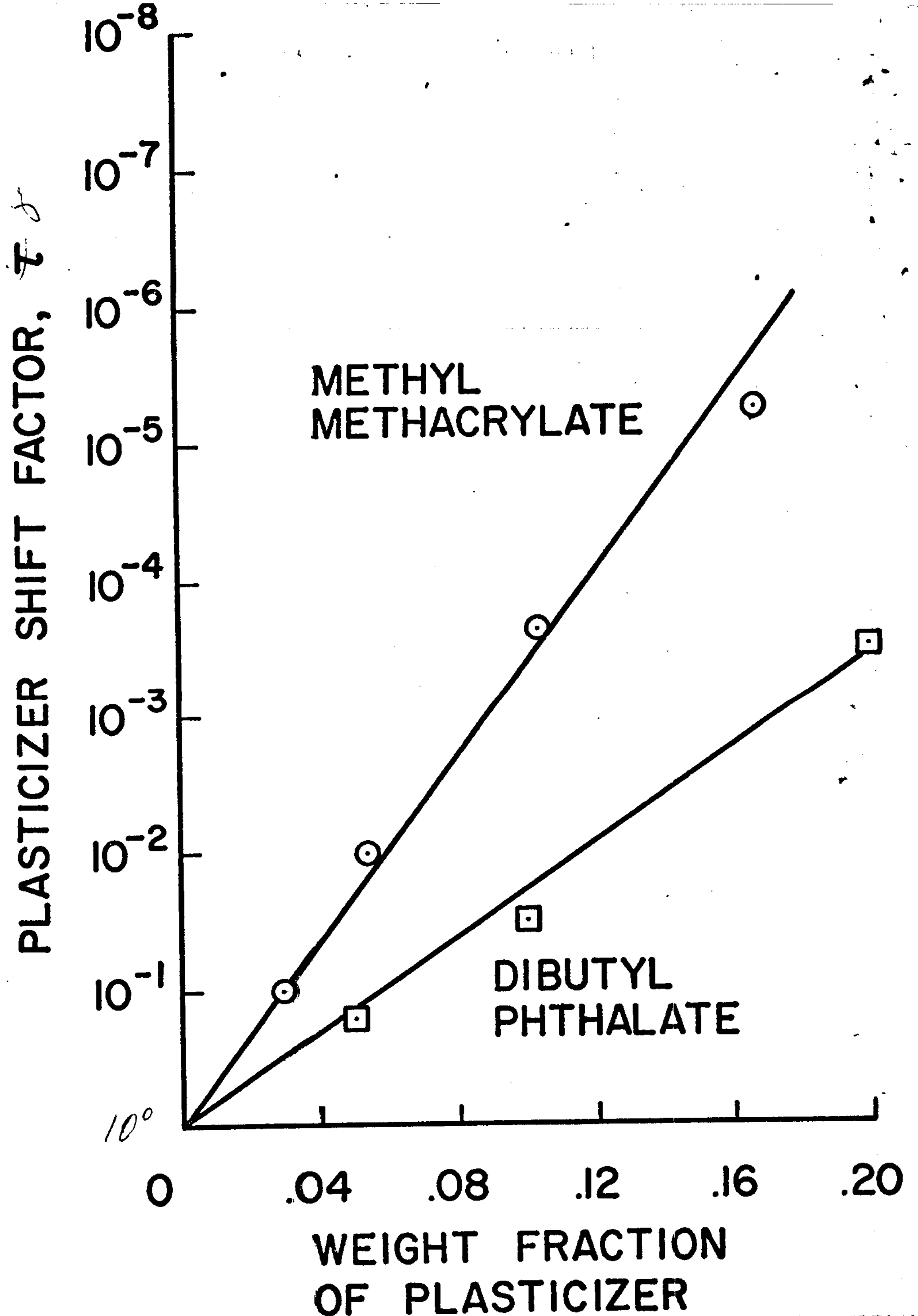

Figure 10. - The plasticizer shift factor for polymethylmethacrylate as a function of weight fraction of plasticizer for derivation of equation 3.